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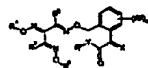
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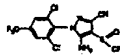


(54) Title: FUNGICIDE MIXTURES BASED ON TRIPLE OXIME ETHER DERIVATIVES AND INSECTICIDES

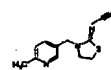
(54) Bezeichnung: FUNGIZIDE MISCHUNGEN AUF DER BASIS VON TRIPELOXIMETHERDERIVATEN UND INSEKTIZIDEN



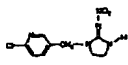
(I)



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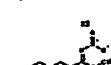
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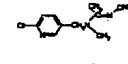
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(V)



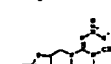
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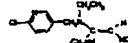
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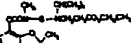
(VIII)



(IX)



(X)



(XI)

(57) Abstract

The invention relates to a) phenylacetic acid derivatives of formula (I) in which the substituents and the index have the meanings cited in the description, and to the salts thereof, and to b) at least one compound of formulas (II) to (XI) in a synergistically effective quantity.

(57) Zusammenfassung

a) Phenyllessigsäurederivate der Formel (I), in der die Substituenten und der Index die in der Beschreibung genannte Bedeutung haben, sowie deren Salze, und b) mindestens eine Verbindung der Formeln (II) bis (XI) in einer synergistisch wirksamen Menge.

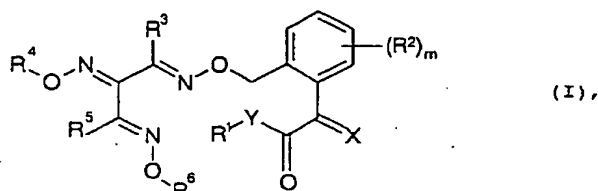
Fungicidal mixtures based on tris(oxime ether) derivatives and insecticides

5 The present invention relates to mixtures for controlling harmful fungi and insects, which comprises

a) phenylacetic acid derivatives of the formula I

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in which the substituents and the index have the following meaning:

X is NOCH₃, CHOCH₃ or CHCH₃;

25

Y is oxygen or NR;

R¹, R independently of one another are each hydrogen or C₁-C₄-alkyl;

30

R² is cyano, nitro, trifluoromethyl, halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy;

m is 0, 1 or 2, where the radicals R² may be different if m is 2;

35

R³ is hydrogen, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl or C₃-C₆-cycloalkyl;

40

R⁴, R⁵ independently of one another are each hydrogen,

are C₁-C₁₀-alkyl, C₃-C₆-cycloalkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₁-C₁₀-alkylcarbonyl, C₂-C₁₀-alkenylcarbonyl, C₃-C₁₀-alkynylcarbonyl or C₁-C₁₀-alkylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl,



aminothiocarbonyl, halogen, C₁-C₆-alkyl,
 C₁-C₆-haloalkyl, C₁-C₆-alkylsulfonyl,
 C₁-C₆-alkylsulfoxyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy,
 C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio, C₁-C₆-alkylamino,
 di-C₁-C₆-alkylamino, C₁-C₆-alkylaminocarbonyl,
 di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 C₂-C₆-alkenyloxy, C₃-C₆-cycloalkyl, C₃-C₆-cycloalkyloxy,
 heterocyclyl, heterocycliloxy, benzyl, benzyloxy, aryl,
 aryloxy, arylthio, hetaryl, hetaryloxy and hetarylthio,
 where the cyclic groups for their part may be partially
 or fully halogenated or may carry one to three of the
 following groups: cyano, nitro, hydroxyl, mercapto,
 amino, carboxyl, aminocarbonyl, aminothiocarbonyl,
 halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl,
 C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfoxyl,
 C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy,
 C₁-C₆-alkyloxycarbonyl, C₁-C₆-alkylthio,
 C₁-C₆-alkylamino, di-C₁-C₆-alkylamino,
 C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,
 arylthio, hetaryl, hetaryloxy, hetarylthio or
 C(=NOR⁷)-A_n-R⁸;

are aryl, arylcarbonyl, arylsulfonyl, hetaryl,
 hetarylcarbonyl or hetarylsulfonyl, where these
 radicals may be partially or fully halogenated or may
 carry one to three of the following groups: cyano,
 nitro, hydroxyl, mercapto, amino, carboxyl,
 aminocarbonyl, aminothiocarbonyl, halogen, C₁-C₆-alkyl,
 C₁-C₆-haloalkyl, C₁-C₆-alkylcarbonyl,
 C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfoxyl,
 C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy,
 C₁-C₆-alkyloxycarbonyl, C₁-C₆-alkylthio,
 C₁-C₆-alkylamino, di-C₁-C₆-alkylamino,
 C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,
 hetaryl, hetaryloxy or C(=NOR⁷)-A_n-R⁸;

R⁵ is hydrogen,



is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, where the hydrocarbon radicals of these groups may be partially or fully halogenated or may carry one to three of the following radicals: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl, C₁-C₆-alkylaminothiocarbonyl, di-C₁-C₆-alkylaminothiocarbonyl, C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfoxyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₆-alkenyloxy, C₃-C₆-cycloalkyl, C₃-C₆-cycloalkyloxy, heterocyclyl, heterocyclyloxy, aryl, aryloxy, aryl-C₁-C₄-alkoxy, arylthio, aryl-C₁-C₄-alkylthio, hetaryl, hetaryloxy, hetaryl-C₁-C₄-alkoxy, hetarylthio, hetaryl-C₁-C₄-alkylthio, where the cyclic radicals for their part may be partially or fully halogenated and/or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfoxyl, C₁-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl, C₁-C₆-alkylaminothiocarbonyl, di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy, hetarylthio and C(=NOR⁷)-A_n-R⁸;

is C₃-C₆-cycloalkyl, C₃-C₆-cycloalkenyl, heterocyclyl, aryl, hetaryl, where the cyclic radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfoxyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl, C₁-C₆-alkylaminothiocarbonyl, di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, hetaryl and hetaryloxy;



where

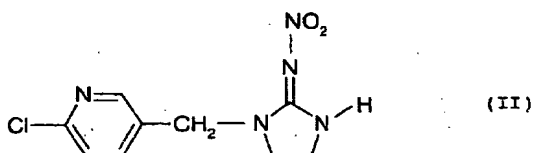
- 5 A is oxygen, sulfur or nitrogen and where the nitrogen
 carries hydrogen or C₁-C₆-alkyl;
- n is 0 or 1;
- R⁷ is hydrogen or C₁-C₆-alkyl and
- 10 R⁸ is hydrogen or C₁-C₆-alkyl,
- and their salts,

and

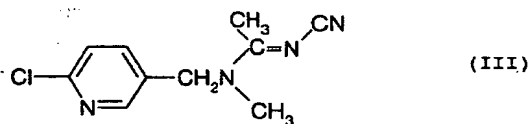
- 15 b) at least one insecticide selected from insecticides of the
 formulae II to XI

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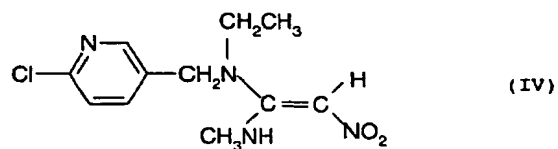


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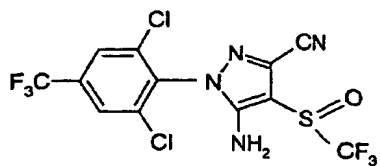


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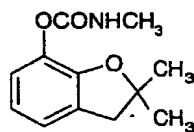


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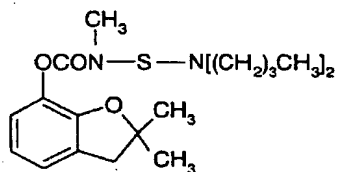
(V)

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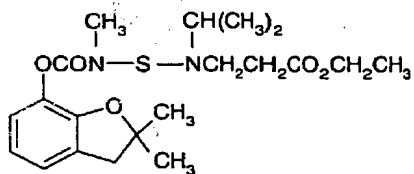
(VI)

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(VII)

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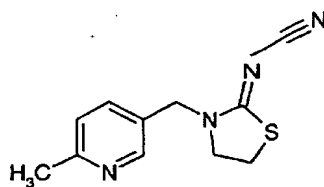


(VIII)

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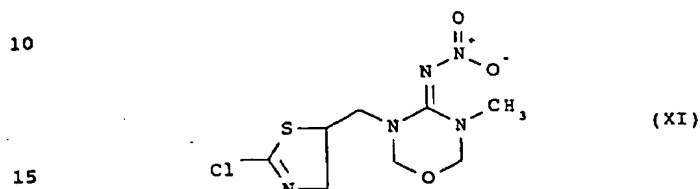
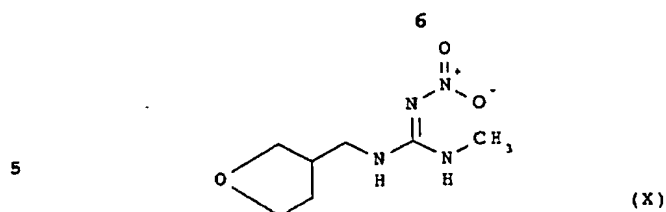
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(IX)

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It is an object of the present invention to provide mixtures which, on the one hand, have good fungicidal activity, in particular against fungal diseases in rice and, on the other hand, good insecticidal activity. Since in the climatic regions in which rice is cultivated, harmful insects are usually also encountered in great numbers, a combination of fungicidal and insecticidal activity is desirable.

25 We have found that this object is achieved by the mixtures claimed in claim 1.

The compounds of the formula I and their preparation are known per se and described in the literature (WO 97/15,552).

The insecticides of the formulae II to XI are also known and described in the literature. Additionally, they are commercially available under the trade names mentioned below in brackets:

II: EP-A 192,060, common name: imidacloprid (trade name: Admire®, Gaucho®, from Bayer);

40 III: common name: acetamiprid (trade name: Mospilan®, from Nippon Soda);

IV: CAS RN 120738-89-8, common name: nitenpyram (trade name: Bestgard®, from Takeda Chemicals);



- V: Colliot et al., Proc. Br. Conf. Dis. 1, (1992), 29, common name: fipronil (trade name: Regent®, from Rhone-Poulenc);
- VI: US 3,474,170; US 3,474,171 and DE-C 1,493,646; common name: carbofuran (trade name Curaterr®, from Bayer; Furadan®, from FMC);
- VII: Proc. Br. Crop Prot. Conf. 2 (1979), 557, common name: carbosulfan (trade name: Marshall®, from FMC);
- VIII: FR-A 2,489,329; Proc. Int. Congr. Plant Prot. 10th, 2 (1983), 360, common name: benfuracarb (trade name: Oncol®, from Otsuka; Furacon®, from Siapa Chem.);
- IX: CAS RN 111 988-49-9, common name: thiacloprid (development product from Bayer);
- X: Proc. of the 1998 Brighton Conference "Pests and Diseases", Vol. 1, pp. 21-26 (MTI 446, from Mitsui);
- XI: Proc. of the Brighton Conference on Pests and Diseases, Vol. 1, pp. 27-36 (CGA 293 343, from Novartis).

Owing to their C=C and C=N double bonds, the preparation of the compounds I may yield E/Z isomer mixtures which can be separated into the individual compounds in a customary manner, for example by crystallization or chromatography.

However, if the synthesis yields isomer mixtures, a separation is generally not necessarily required since in some cases the individual isomers can be converted into one another during the preparation for use or upon use (for example under the action of light, acids or bases). Similar conversions may also occur after use, for example in the treatment of plants in the treated plant or in the harmful fungus or animal pest to be controlled.

With regard to the C=X double bond, preference is given to the E isomers of the compounds I (configuration based on the -OCH₃ or the -CH₃ group in relation to the -CO₂R¹ group) with respect to their activity.

With regard to the -C(R³)=NOCH₂- double bond, preference is given to the cis isomers of the compounds I (configuration based on the radical R³ in relation to the -OCH₂- group) with respect to their activity.



In the definitions of the compounds I given at the outset, collective terms were used which generally represent the following groups:

5 Halogen: fluorine, chlorine, bromine and iodine;

Alkyl: straight-chain or branched alkyl groups having 1 to 4, 6 or 10 carbon atoms, for example C₁-C₆-alkyl such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl,

10 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 15 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;

20 Haloalkyl: straight-chain or branched alkyl groups having 1 to 6 carbon atoms, it being possible for some or all of the hydrogen atoms in these groups to be replaced by halogen atoms as mentioned above, for example C₁-C₂-haloalkyl, such as chloromethyl, dichloromethyl, trichloromethyl, fluoromethyl,

25 difluoromethyl, trifluoromethyl, chlorodifluoromethyl, dichlorodifluoromethyl, chlorodifluoroethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl and 30 pentafluoroethyl;

Cycloalkyl: monocyclic alkyl groups having 3 to 6 carbon ring members, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl;

35

Alkenyl: straight-chain or branched alkenyl groups having 2 to 6 or 10 carbon atoms and a double bond in any position, for example C₂-C₆-alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl,

40 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 45 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl,



3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl,
 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl,
 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl,
 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl,
 5 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl,
 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl,
 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl,
 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl,
 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl,
 10 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl,
 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl,
 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl,
 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl,
 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl,
 15 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl,
 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl,
 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;

Alkynyl: straight-chain or branched alkynyl groups having 2 to 10
 20 carbon atoms and a triple bond in any position, for example
 C₂-C₆-alkynyl, such as ethynyl, 2-propynyl, 2-butylnyl, 3-butylnyl,
 1-methyl-2-propynyl, 2-pentylnyl, 3-pentylnyl, 4-pentylnyl,
 1-methyl-2-butylnyl, 1-methyl-3-butylnyl, 2-methyl-3-butylnyl,
 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 2-hexynyl,
 25 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentylnyl,
 1-methyl-3-pentylnyl, 1-methyl-4-pentylnyl, 2-methyl-3-pentylnyl,
 2-methyl-4-pentylnyl, 3-methyl-4-pentylnyl, 4-methyl-2-pentylnyl,
 1,1-dimethyl-2-butylnyl, 1,1-dimethyl-3-butylnyl,
 1,2-dimethyl-3-butylnyl, 2,2-dimethyl-3-butylnyl,
 30 1-ethyl-2-butylnyl, 1-ethyl-3-butylnyl, 2-ethyl-3-butylnyl and
 1-ethyl-1-methyl-2-propynyl;

Heterocyclyl or heterocyclyloxy, heterocyclylthio and
 heterocyclylamino: three- to six-membered saturated or partially
 35 unsaturated mono- or polycyclic heterocycles which contain one to
 three heteroatoms selected from a group consisting of oxygen,
 nitrogen and sulfur and which are attached to the skeleton
 directly or (heterocyclyloxy) via an oxygen atom or
 (heterocyclylthio) via a sulfur atom or (heterocyclylamino) via a
 40 nitrogen atom, such as, for example, 2-tetrahydrofuranyl,
 oxiranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl,
 3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl,
 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl,
 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl,
 45 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl,
 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl,
 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl,



- 4-imidazolidinyl, 1,2,4-oxadiazolidin-3-yl,
 1,2,4-oxadiazolidin-5-yl, 1,2,4-thiadiazolidin-3-yl,
 1,2,4-thiadiazolidin-5-yl, 1,2,4-triazolidin-3-yl,
 1,3,4-oxadiazolidin-2-yl, 1,3,4-thiadiazolidin-2-yl,
 5 1,3,4-triazolidin-2-yl, 2,3-dihydrofur-2-yl, 2,3-dihydrofur-3-yl,
 2,3-dihydrofur-4-yl, 2,3-dihydrofur-5-yl, 2,5-dihydrofur-2-yl,
 2,5-dihydrofur-3-yl, 2,3-dihydrothien-2-yl,
 2,3-dihydrothien-3-yl, 2,3-dihydrothien-4-yl,
 2,3-dihydrothien-5-yl, 2,5-dihydrothien-2-yl,
 10 2,5-dihydrothien-3-yl, 2,3-dihydropyrrol-2-yl,
 2,3-dihydropyrrol-3-yl, 2,3-dihydropyrrol-4-yl,
 2,3-dihydropyrrol-5-yl, 2,5-dihydropyrrol-2-yl,
 2,5-dihydropyrrol-3-yl, 2,3-dihydroisoxazol-3-yl,
 2,3-dihydroisoxazol-4-yl, 2,3-dihydroisoxazol-5-yl,
 15 4,5-dihydroisoxazol-3-yl, 4,5-dihydroisoxazol-4-yl,
 4,5-dihydroisoxazol-5-yl, 2,5-dihydroisothiazol-3-yl,
 2,5-dihydroisothiazol-4-yl, 2,5-dihydroisothiazol-5-yl,
 2,3-dihydroisopyrazol-3-yl, 2,3-dihydroisopyrazol-4-yl,
 2,3-dihydroisopyrazol-5-yl, 4,5-dihydroisopyrazol-3-yl,
 20 4,5-dihydroisopyrazol-4-yl, 4,5-dihydroisopyrazol-5-yl,
 2,5-dihydroisopyrazol-3-yl, 2,5-dihydroisopyrazol-4-yl,
 2,5-dihydroisopyrazol-5-yl, 2,3-dihydrooxazol-3-yl,
 2,3-dihydrooxazol-4-yl, 2,3-dihydrooxazol-5-yl,
 4,5-dihydrooxazol-3-yl, 4,5-dihydrooxazol-4-yl,
 25 4,5-dihydrooxazol-5-yl, 2,5-dihydrooxazol-3-yl,
 2,5-dihydrooxazol-4-yl, 2,5-dihydrooxazol-5-yl,
 2,3-dihydrothiazol-2-yl, 2,3-dihydrothiazol-4-yl,
 2,3-dihydrothiazol-5-yl, 4,5-dihydrothiazol-2-yl,
 4,5-dihydrothiazol-4-yl, 4,5-dihydrothiazol-5-yl,
 30 2,5-dihydrothiazol-2-yl, 2,5-dihydrothiazol-4-yl,
 2,5-dihydrothiazol-5-yl, 2,3-dihydroimidazol-2-yl,
 2,3-dihydroimidazol-4-yl, 2,3-dihydroimidazol-5-yl,
 4,5-dihydroimidazol-2-yl, 4,5-dihydroimidazol-4-yl,
 4,5-dihydroimidazol-5-yl, 2,5-dihydroimidazol-2-yl,
 35 2,5-dihydroimidazol-4-yl, 2,5-dihydroimidazol-5-yl,
 2-morpholinyl, 3-morpholinyl, 2-piperidinyl, 3-piperidinyl,
 4-piperidinyl, 3-tetrahydropyridazinyl, 4-tetrahydropyridazinyl,
 2-tetrahydropyrimidinyl, 4-tetrahydropyrimidinyl,
 5-tetrahydropyrimidinyl, 2-tetrahydropyrazinyl,
 40 1,3,5-tetrahydrotriazin-2-yl, 1,2,4-tetrahydrotriazin-3-yl,
 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl, 2-tetrahydropyranyl,
 1,3-dioxolan-2-yl, 3,4,5,6-tetrahydropyridin-2-yl,
 4H-1,3-thiazin-2-yl, 4H-3,1-benzothiazin-2-yl,
 1,1-dioxo-2,3,4,5-tetrahydrothien-2-yl, 2H-1,4-benzothiazin-3-yl,
 45 2H-1,4-benzoxazin-3-yl, 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl;



Aryl or aryloxy, arylthio, arylcarbonyl and arylsulfonyl: aromatic mono- or polycyclic hydrocarbon radicals which are attached to the skeleton directly or (aryloxy) via an oxygen atom (-O-) or (arylthio) a sulfur atom (-S-), (arylcarbonyl) via a carbonyl group (-CO-) or (arylsulfonyl) via a sulfonyl group (-SO₂-), for example phenyl, naphthyl and phenanthrenyl or phenyloxy, naphthyloxy and phenanthrenyloxy and the corresponding carbonyl and sulfonyl radicals;

- 10 Hetaryl or hetaryloxy, hetarylthio, hetarylcarbonyl and hetarylsulfonyl: aromatic mono- or polycyclic radicals which, beside carbon ring members, can additionally contain one to four nitrogen atoms or one to three nitrogen atoms and one oxygen or one sulfur atom or one oxygen or one sulfur atom and which are
- 15 attached to the skeleton directly or (hetaryloxy) via an oxygen atom (-O-) or (hetarylthio) a sulfur atom (-S-), (hetarylcarbonyl) via a carbonyl group (-CO-) or (hetarylsulfonyl) via a sulfonyl group (-SO₂-), for example
- 20 - 5-membered heteroaryl, containing one to three nitrogen atoms: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to three nitrogen atoms as ring members, for example 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-imidazolyl, 4-imidazolyl,
- 25 1,2,4-triazol-3-yl and 1,3,4-triazol-2-yl;
- 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or one sulfur atom: 5-membered heteroaryl
- 30 groups which, beside carbon atoms, can contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or sulfur atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl,
- 35 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl,
- 40 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,3,4-triazol-2-yl;
- benzo-fused 5-membered heteroaryl, containing one to three
- 45 nitrogen atoms or one nitrogen atom and/or one oxygen or sulfur atom: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms or one



to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or one sulfur atom as ring members, and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member may be bridged by a buta-1,3-dien-1,4-diyl group;

5

- 5-membered heteroaryl bonded via nitrogen and containing one to four nitrogen atoms, or benzo-fused 5-membered heteroaryl, bonded via nitrogen and containing one to three nitrogen atoms: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms and one to three nitrogen atoms, respectively, as ring members, and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member can be bridged by a buta-1,3-dien-1,4-diyl group, these rings being attached to the skeleton via one of the nitrogen ring members;

10

15

- 6-membered heteroaryl containing one to three and one to four nitrogen atoms, respectively: 6-membered heteroaryl groups which, beside carbon atoms, can contain one to three and one to four nitrogen atoms, respectively, as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl, 1,2,4-triazin-3-yl and 1,2,4,5-tetrazin-3-yl;

25

- benzo-fused 6-membered heteroaryl containing one to four nitrogen atoms: 6-membered heteroaryl groups in which two adjacent carbon ring members can be bridged by a buta-1,3-dien-1,4-diyl group, for example quinoline, isoquinoline, quinazoline and quinoxaline,

30

and the corresponding oxy, thio, carbonyl or sulfonyl groups.

35 Hetaryl-amino: aromatic mono- or polycyclic radicals which, beside carbon ring members, can additionally contain one to four nitrogen atoms or one to three nitrogen atoms and one oxygen or one sulfur atom and which are attached to the skeleton via a nitrogen atom.

40

The specification "partially or fully halogenated" is meant to express that some or all of the hydrogen atoms in the groups thus characterized may be replaced by identical or different halogen atoms as mentioned above.



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With respect to their biological activity, preference is given to compounds of the formula I in which m is 0.

Likewise, preference is given to compounds of the formula I in which R¹ is methyl.

Besides, preference is given to compounds I in which R³ is hydrogen, cyano, cyclopropyl, methyl, ethyl, 1-methylethyl or CF₃.

10 Moreover, preference is given to compounds I in which R³ is methyl.

Besides, preference is given to compounds I in which R³ is cyano.

15 Furthermore, preference is given to compounds I in which R³ is cyclopropyl.

Additionally, preference is given to compounds I in which R³ is CF₃.

20 Additionally, preference is given to compounds I in which R⁵ is hydrogen, cyclopropyl, methyl, ethyl, isopropyl, unsubstituted or substituted aryl or hetaryl.

25 Moreover, preference is given to compounds I in which R⁵ is methyl.

Additionally, preference is given to compounds I in which R⁵ is ethyl.

30 Moreover, preference is given to compounds I in which R⁵ is isopropyl.

Moreover, preference is given to compounds I in which R⁵ is cyclopropyl.

35 Moreover, preference is given to compounds I in which R⁵ is CF₃.

40 Additionally, preference is given to compounds I in which R⁵ is unsubstituted or substituted aryl or hetaryl.

Additionally, preference is given to compounds I in which R⁵ is unsubstituted or substituted pyridyl, pyrimidyl, pyrazinyl, pyridazinyl or triazinyl.

45



Additionally, preference is given to compounds I in which R⁵ is unsubstituted or substituted furyl, thienyl or pyrrolyl.

Additionally, preference is given to compounds I in which R⁵ is unsubstituted or substituted oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, pyrazolyl or imidazolyl.

Additionally, preference is given to compounds I in which R¹ is unsubstituted or substituted oxadiazolyl, thiadiazolyl or triazolyl.

Moreover, preference is given to compounds I in which R⁵ is phenyl which is unsubstituted or carries one or two of the following groups: nitro, cyano, hydroxyl, amino, aminocarbonyl, aminothiocarbonyl, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylamino, di-C₁-C₄-alkylamino, C₁-C₄-alkylsulfonyl, C₁-C₄-alkoxycarbonyl, C₁-C₄-alkylaminocarbonyl or di-C₁-C₄-alkylaminocarbonyl.

Moreover, preference is given to compounds I in which R⁴ is hydrogen, C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, allyl, arylalkyl, hetarylalkyl, aryloxyalkyl, hetaryloxyalkyl, aryl or hetaryl.

Additionally, preference is given to compounds I in which R⁴ is C₁-C₆-alkyl.

Further preferred compounds I are disclosed in WO 97/15,552.

The compounds I which are contained in the mixtures according to the invention have excellent activity against a broad range of phytopathogenic fungi, in particular against fungi from the classes of the Ascomycetes, Deuteromycetes, Phycomycetes and Basidiomycetes.

They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable species (for example cucumbers, beans, tomatoes, potatoes and cucurbits), barley, grass, oats, bananas, coffee, maize, fruit species, rice, rye, soya, grapevine, wheat, ornamentals, sugar cane, and a variety of seeds.

They are particularly suitable for controlling the following phytopathogenic fungi: Erysiphe graminis (powdery mildew) in cereals, Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits, Podosphaera leucotricha in apples, Uncinula necator in grapevines, Puccinia species in cereals, Rhizoctonia species in



cotton, rice and lawns, *Ustilago* species in cereals and sugar cane, *Venturia inaequalis* (scab) in apples, *Helminthosporium* species in cereals and rice, *Septoria nodorum* in wheat, *Botrytis cinera* [sic] (gray mold) in strawberries, vegetables, ornamentals and grapevines, *Cercospora arachidicola* in groundnuts, *Pseudocercospora herpotrichoides* in wheat and barley, *Pyricularia oryzae* in rice and lawns, *Phytophthora infestans* in potatoes and tomatoes, *Plasmopara viticola* in grapevines, *Pseudoperonospora* species in hops and cucumbers, *Alternaria* species in vegetables and fruit, *Mycosphaerella* species in bananas and *Fusarium* and *Verticillium* species.

The compounds of the formulae II to XI are used for controlling animal pests from the class of the insects, arachnids and nematodes. They can be employed in crop protection and in the hygiene, stored-product and veterinary sector for controlling animal pests. In particular, they are suitable for controlling the following animal pests:

- 20 • insects from the order of the lepidopterans (Lepidoptera), e.g. *Agrotis ypsilon*, *Agrotis segetum*, *Alabama argillacea*, *Anticarsia gemmatilis*, *Argyresthia conjugella*, *Autographa gamma*, *Bupalus piniarius*, *Cacoecia murinana*, *Capua reticulana*, *Cheimatobia brumata*, *Choristoneura fumiferana*, *Choristoneura occidentalis*, *Cirphis unipuncta*, *Cydia pomonella*, *Dendrolimus pini*, *Diaphania nitidalis*, *Diatraea grandiosella*, *Earias insulana*, *Elasmopalpus lignosellus*, *Eupoecilia ambiguella*, *Evetria bouliana*, *Feltia subterranea*, *Galleria mellonella*, *Grapholitha funebrana*, *Grapholitha molesta*, *Heliothis armigera*, *Heliothis virescens*, *Heliothis zea*, *Hellula undalis*, *Hibernia defoliaria*, *Hyphantria cunea*, *Hyponomeuta malinellus*, *Keiferia lycopersicella*, *Lambdina fiscellaria*, *Laphygma exigua*, *Leucoptera coffeella*, *Leucoptera scitella*, *Lithocolletis blanchardella*, *Lobesia botrana*, *Loxostege sticticalis*, *Lymantria dispar*, *Lymantria monacha*, *Lyonetia clerkella*, *Malacosoma neustria*, *Mamestra brassicae*, *Orgyia pseudotsugata*, *Ostrinia nubilalis*, *Panolis flammea*, *Pectinophora gossypiella*, *Peridroma saucia*, *Phalera bucephala*, *Phthorimaea operculella*, *Phyllocnistis citrella*, *Pieris brassicae*, *Plathypena scabra*, *Plutella xylostella*, *Pseudoplusia includens*, *Rhyacionia frustrana*, *Scrobipalpula absoluta*, *Sitotroga cerealella*, *Sparganothis pilleriana*, *Spodoptera frugiperda*, *Spodoptera littoralis*, *Spodoptera litura*, *Thaumatopoea pityocampa*, *Tortrix viridana*, *Trichoplusia ni* and *Zeiraphera canadensis*,
- 45 • beetles (Coleoptera), e.g. *Agrius sinuatus*, *Agriotes lineatus*, *Agriotes obscurus*, *Amphimallus solstitialis*, *Anisandrus dispar*,



- Anthonomus grandis, Anthonomus pomorum, Atomaria linearis,
 Blastophagus piniperda, Blitophaga undata, Bruchus rufimanus,
 Bruchus pisorum, Bruchus lentis, Byctiscus betulae, Cassida
 nebulosa, Cerotoma trifurcata, Ceuthorrhynchus assimilis,
 5 Ceuthorrhynchus napi, Chaetocnema tibialis, Conoderus
 vespertinus, Crioceris asparagi, Diabrotica longicornis,
 Diabrotica 12-punctata, Diabrotica virgifera, Epilachna
 varivestis, Epitrix hirtipennis, Eutinobothrus brasiliensis,
 Hylobius abietis, Hypera brunneipennis, Hypera postica, Ips
 10 decemlineata, Limonius californicus, Lissorhoptrus oryzophilus,
 Melanotus communis, Meligethes aeneus, Melolontha hippocastani,
 Melolontha melolontha, Oulema oryzae, Otiorrhynchus sulcatus,
 Otiorrhynchus ovatus, Phaedon cochleariae, Phyllotreta
 15 chrysocephala, Phyllophaga sp., Phyllopertha horticola,
 Phyllotreta nemorum, Phyllotreta striolata, Popillia japonica,
 Sitona lineatus and Sitophilus granaria,
- dipterans (Diptera), e.g. Aedes aegypti, Aedes vexans,
 20 Anastrepha ludens, Anopheles maculipennis, Ceratitis capitata,
 Chrysomya bezziana, Chrysomya hominivorax, Chrysomya
 macellaria, Contarinia sorghicola, Cordylobia anthropophaga,
 Culex pipiens, Dacus cucurbitae, Dacus oleae, Dasineura
 brassicae, Fannia canicularis, Gasterophilus intestinalis,
 25 Glossina morsitans, Haematobia irritans, Haplodiplosis
 equestris, Hylemyia platura, Hypoderma lineata, Liriomyza
 sativae, Liriomyza trifolii, Lucilia cuprina, Lucilia sericata,
 Lycoria pectoralis, Mayetiola destructor, Musca domestica,
 30 Muscina stabulans, Oestrus ovis, Oscinella frit, Pegomya
 hysocyami, Phorbia antiqua, Phorbia brassicae, Phorbia coarctata,
 Rhagoletis cerasi, Rhagoletis pomonella, Tabanus bovinus, Tipula
 oleracea and Tipula paludosa,
- thrips (Thysanoptera), e.g. Frankliniella fusca, Frankliniella
 35 occidentalis, Frankliniella tritici, Scirtothrips citri, Thrips
 oryzae, Thrips palmi and Thrips tabaci,
- hymenopterans (Hymenoptera), e.g. Athalia rosae, Atta
 cephalotes, Atta sexdens, Atta texana, Hoplocampa minuta,
 40 Hoplocampa testudinea, Monomorium pharaonis, Solenopsis
 geminata and Solenopsis invicta,
- heteropterans (Heteroptera), e.g. Acrosternum hilare, Blissus
 leucopterus, Cyrtopeltis notatus, Dysdercus cingulatus,
 Dysdercus intermedius, Eurygaster integriceps, Euschistus
 impictiventris, Leptoglossus phyllopus, Lygus lineolaris, Lygus



pratensis, *Nezara viridula*, *Piesma quadrata*, *Solubea insularis* and *Thyanta perditor*,

- homopterans (Homoptera), e.g. *Acyrtosiphon onobrychis*, *Adelges laricis*, *Aphidula nasturtii*, *Aphis fabae*, *Aphis pomi*, *Aphis sambuci*, *Brachycaudus cardui*, *Brevicoryne brassicae*, *Cerosiphia gossypii*, *Dreyfusia nordmannianae*, *Dreyfusia piceae*, *Dysaphis radicola*, *Dysaulacorthum pseudosolani*, *Empoasca fabae*, *Macrosiphum avenae*, *Macrosiphum euphorbiae*, *Macrosiphon rosae*, *Megoura viciae*, *Metopolophium dirhodum*, *Myzodes persicae*, *Myzus cerasi*, *Nilaparvata lugens*, *Pemphigus bursarius*, *Perkinsiella saccharicida*, *Phorodon humuli*, *Psylla mali*, *Psylla piri*, *Rhopalomyzus ascalonicus*, *Rhopalosiphum maidis*, *Sappaphis mala*, *Sappaphis mali*, *Schizaphis graminum*, *Schizoneura lanuginosa*, *Trialeurodes vaporariorum* and *Viteus vitifolii*,
- termites (Isoptera), e.g. *Calotermes flavicollis*, *Leucotermes flavipes*, *Reticulitermes lucifugus* und *Termes natalensis*,
- 20 • orthopterans (Orthoptera), e.g. *Acheta domestica*, *Blatta orientalis*, *Blattella germanica*, *Forficula auricularia*, *Gryllotalpa gryllotalpa*, *Locusta migratoria*, *Melanoplus bivittatus*, *Melanoplus femur-rubrum*, *Melanoplus mexicanus*, *Melanoplus sanguinipes*, *Melanoplus spretus*, *Nomadacris septemfasciata*, *Periplaneta americana*, *Schistocerca americana*, *Schistocerca peregrina*, *Stauronotus maroccanus* and *Tachycines asynamorus*,
- 30 • Arachnoidea, such as arachnids (Acarina), e.g. *Amblyomma americanum*, *Amblyomma variegatum*, *Argas persicus*, *Boophilus annulatus*, *Boophilus decoloratus*, *Boophilus microplus*, *Brevipalpus phoenicis*, *Bryobia praetiosa*, *Dermacentor silvarum*, *Eotetranychus carpini*, *Eriophyes sheldoni*, *Hyalomma truncatum*, *Ixodes ricinus*, *Ixodes rubicundus*, *Ornithodoros moubata*,
- 35 *Otobius megnini*, *Paratetranychus pilosus*, *Dermanyssus gallinae*, *Phyllocoptura oleivora*, *Polyphagotarsonemus latus*, *Psoroptes ovis*, *Rhipicephalus appendiculatus*, *Rhipicephalus evertsi*, *Sarcoptes scabiei*, *Tetranychus cinnabarinus*, *Tetranychus kanzawai*, *Tetranychus pacificus*, *Tetranychus telarius* and
- 40 *Tetranychus urticae*,
- nematodes such as root knot nematodes, e.g. *Meloidogyne hapla*, *Meloidogyne incognita*, *Meloidogyne javanica*, cyst-forming nematodes, e.g. *Globodera rostochiensis*, *Heterodera avenae*, *Heterodera glycines*, *Heterodera schachtii*, *Heterodera trifolii*,
- 45 stem eelworms and foliar nematodes, e.g. *Belonolaimus longicaudatus*, *Ditylenchus destructor*, *Ditylenchus dipsaci*, *Heliocotylenchus multicinctus*, *Longidorus elongatus*, *Radopholus*



similis, *Rotylenchus robustus*, *Trichodorus primitivus*,
Tylenchorhynchus claytoni, *Tylenchorhynchus dubius*,
Pratylenchus neglectus, *Pratylenchus penetrans*, *Pratylenchus*
curvatus and *Pratylenchus goodeyi*.

5 The application rate of active ingredient for controlling animal pests is under field conditions usually from 0.01 to 2.0, preferably 0.02 to 1.0, kg/ha.

10 The mixtures according to the invention are particularly preferably utilizable for controlling plant diseases and harmful insects in rice.

The compounds I and at least one of the compounds II to XI can be
 15 applied simultaneously, either together or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the control results.

Depending on the nature of the desired effect, the application
 20 rates of the mixtures according to the invention are, in particular in agricultural crops, from 0.01 to 8 kg/ha, preferably from 0.1 to 5 kg/ha, in particular from 0.5 to 3.0 kg/ha.

25 In the case of the compounds I, the application rates are from 0.01 to 2.5 kg/ha, preferably from 0.05 to 2.5 kg/ha, in particular from 0.1 to 1.0 kg/ha.

For seed treatment, the application rates of the mixture are
 30 generally from 0.001 to 250 g/kg of seed, preferably 0.01 to 100 g/kg, in particular 0.01 to 50 g/kg.

If phytopathogenic harmful fungi are to be controlled, the
 separate or joint application of the compounds I and at least one
 35 of the compounds II to XI or of the mixtures of the compounds I and at least one of compounds II to XI is effected by spraying or dusting the seeds, the plants or the soils before or after sowing the plants, or before or after plant emergence.

40 The mixtures according to the invention can be formulated for example in the form of ready-to-spray solutions, powders and suspensions or in the form of highly concentrated aqueous, oily or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, and
 45 applied by spraying, atomizing, dusting, broadcasting or watering. The use form depends on the intended purpose; in any case, it should ensure as fine and uniform a distribution as



possible of the mixture according to the invention.

The formulations are prepared in a known manner, for example by expanding the active ingredient with solvents and/or carriers, if 5 desired by use of emulsifiers and dispersants. If the diluent used is water, it is also possible to use other organic solvents as auxiliary solvents. Suitable auxiliaries are essentially: solvents, such as aromatics (for example xylene), chlorinated aromatics (for example chlorobenzenes), paraffins (for example 10 mineral oil fractions), alcohols (for example methanol, butanol), ketones (for example cyclohexanone), amines (for example ethanolamine, dimethylformamide) and water; carriers, such as natural ground minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example finely divided silica, 15 silicates); emulsifiers, such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates), and dispersants, such as lignosulfite waste liquors and methylcellulose.

20 Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, e.g. ligno-, phenol-, naphthalene- and dibutyl-naphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated 25 hexa-, hepta- and octadecanols, or of fatty alcohol glycol ethers; condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- 30 or nonylphenol, alkylphenol or tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or 35 methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or jointly grinding the compounds I and at least one of the compounds II to XI or the mixture of the compounds I and at 40 least one of the compounds II to XI with a solid carrier.

Granules (e.g. coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active ingredient, or active ingredients, to a solid carrier.

45 Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicic acids, silica gels, silicates, talc,



kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, and fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, 5 and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

The formulations generally comprise 0.1 to 95% by weight, 10 preferably 0.5 to 90% by weight, of one of the compounds I and at least one of the compounds II to XI or of the mixture of the compounds I and at least one of the compounds II to XI. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR or HPLC spectrum.

15 The compounds I and at least one of the compounds II to XI, the mixtures or the corresponding formulations are applied by treating the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them with 20 a fungicidally effective amount of the mixture, or of the compounds I and at least one of the compounds II to XI in the case of separate application.

Application can be effected before or after attack by the harmful 25 fungi.

Examples of such preparations comprising the active ingredients are:

- 30 I. A solution of 90 parts by weight of the active ingredients and 10 parts by weight of N-methylpyrrolidone; this solution is suitable for use in the form of microdrops;
- II. A mixture of 20 parts by weight of the active ingredients, 80 parts by weight of xylene, 10 parts by weight of the 35 adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil; a dispersion is obtained by finely distributing the 40 solution in water;
- III. An aqueous dispersion of 20 parts by weight of the active ingredients, 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;
- 45 IV. An aqueous dispersion of 20 parts by weight of the active ingredients, 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction of boiling point 210 to



280°C, and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;

- V. A mixture, ground in a hammer mill, of 80 parts by weight of the active ingredients, 3 parts by weight of the sodium salt of diisobutyl-naphthalene-1-sulfonic acid, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel; a spray mixture is obtained by finely distributing the mixture in water;
- 5
- 10 VI. An intimate mixture of 3 parts by weight of the active ingredients and 97 parts by weight of finely divided kaolin; this dust comprises 3% by weight of active ingredient;
- VII. An intimate mixture of 30 parts by weight of the active ingredients, 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel; this formulation imparts good adhesion to the active ingredient;
- 15
- VIII. A stable aqueous dispersion of 40 parts by weight of the active ingredients, 10 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate, 2 parts by weight of silica gel and 48 parts by weight of water; this dispersion may be diluted further;
- 20
- IX. A stable oily dispersion of 20 parts by weight of the active ingredients, 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 8 parts by weight of fatty alcohol polyglycol ether, 20 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate and 88 parts by weight of a paraffinic mineral oil.
- 25
- 30

The synergistic activity of the mixtures according to the invention can be demonstrated by the following experiments:

- The active ingredients, separately or together, are formulated as
- 35 a 10% emulsion in a mixture of 63% by weight of cyclohexanone and 27% by weight of emulsifier, and correspondingly diluted with water to the desired concentration.

- Evaluation is carried out by determining the infected leaf areas
- 40 in percent. These percentages are converted into efficacies. The efficacy (W) is calculated as follows using Abbot's formula:

$$W = (1 - \alpha) \cdot 100 / \beta$$

- 45 α corresponds to the fungal infection of the treated plants in % and



β corresponds to the fungal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

The expected efficacies of the mixtures of the active ingredients were determined using Colby's formula [R.S. Colby, Weeds 15, 20-22 (1967)] and compared with the observed efficacies.

Colby's formula: $E = x + y - x \cdot y / 100$

- E is the expected efficacy, expressed in % of the untreated control, when using the mixture of the active ingredients A and B at the concentrations a and b
- x is the efficacy, expressed in % of the untreated control, when using active ingredient A at the concentration a
- y is the efficacy, expressed in % of the untreated control, when using active ingredient B at the concentration b

Use Example 1 - Activity against *Pyricularia oryzae* (protective)

- Leaves of potted rice seedlings c.v. "Tai-Nong 67" were sprayed to runoff point with an aqueous preparation of active ingredient which had been prepared from a stock solution comprising 10% of active ingredient, 63% of cyclohexanone and 27% of emulsifier. The following day, the plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae*. The test plants were subsequently placed in climatized chambers at 22-24°C and 95-99% relative atmospheric humidity for 6 days. The extent of the development of the disease on the leaves was then determined visually.
- The visually determined values for the percentage of diseased leaf area were converted into efficacies as percent of the untreated control. An efficacy of 0 means the same disease level as in the untreated control, an efficacy of 100 means 0% disease. The expected efficacies for active ingredient combinations were determined using Colby's formula (Colby, S. R.: "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds 15, pp. 20-22, 1967) and compared with the observed efficacies.
- As component a), use was made of the following compound I':



Table 1:

| Ex. | Active ingredient | Conc. in ppm | Efficacy in % of the untreated control |
|-----|-------------------|-----------------|--|
| 1C | None | (100% diseased) | 0 |
| 2C | Compound I | 2.0 0.5 | 20 0 |
| 3C | Compound II | 2.0 0.5 | 0 0 |
| 4C | Compound V | 2.0 0.5 | 0 0 |

Table 2:

| Ex. | Mixture according to the invention (conc. in ppm) | Observed efficacy | Calculated efficacy *) |
|-----|---|-------------------|------------------------|
| 5 | 2 ppm I' + 2 ppm II | 50 % | 20 % |
| 6 | 0.5 ppm I' + 0.5 ppm II | 30 % | 10 % |
| 7 | 2 ppm I' + 2 ppm V | 40 % | 20 % |
| 8 | 0.5 ppm I' + 0.5 ppm V | 25 % | 10 % |

*1) calculated using Colby's formula

The test results show that for all mixing ratios, the observed efficacy is higher than the efficacy which had been calculated beforehand using Colby's formula.

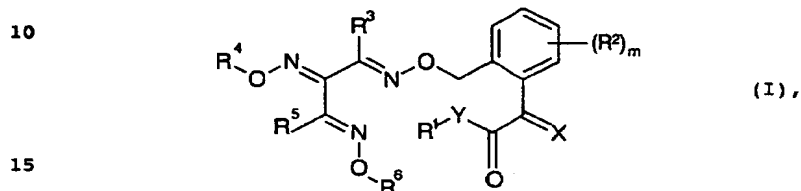
"Comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.



We claim:

1. A mixture for crop protection, comprising as active components

a) phenylacetic acid derivatives of the formula I



in which the substituents and the index have the following meaning:

X NOCH₃, CHOCH₃ or CHCH₃;

Y is oxygen or NR;

R¹, R independently of one another are each hydrogen or C₁-C₄-alkyl;

R² is cyano, nitro, trifluoromethyl, halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy;

m is 0, 1 or 2, where the radicals R² may be different if m is 2;

R³ is hydrogen, cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl or C₃-C₆-cycloalkyl;

R⁴, R⁶ independently of one another are each hydrogen,

are C₁-C₁₀-alkyl, C₃-C₆-cycloalkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, C₁-C₁₀-alkylcarbonyl, C₂-C₁₀-alkenylcarbonyl, C₃-C₁₀-alkynylcarbonyl or C₁-C₁₀-alkylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocabonyl, halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₁-C₆-alkylsulfonyl,



C₁-C₆-alkylsulfoxyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy,
 C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio, C₁-C₆-alkylamino,
 di-C₁-C₆-alkylamino,
 C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 C₂-C₆-alkenyloxy, C₃-C₆-cycloalkyl, C₃-C₆-cycloalkyloxy,
 heterocyclyl, heterocyclyloxy, benzyl, benzyloxy, aryl,
 aryloxy, arylthio, hetaryl, hetaryloxy and hetarylthio,
 where the cyclic groups for their part may be partially
 or fully halogenated or may carry one to three of the
 following groups: cyano, nitro, hydroxyl, mercapto,
 amino, carboxyl, aminocarbonyl, aminothiocarbonyl,
 halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl,
 C₁-C₆-alkylsulfonyl, C₁-C₆-alkylsulfoxyl,
 C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy,
 C₁-C₆-alkyloxycarbonyl, C₁-C₆-alkylthio,
 C₁-C₆-alkylamino, di-C₁-C₆-alkylamino,
 C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,
 arylthio, hetaryl, hetaryloxy, hetarylthio or
 C(=NOR⁷)-A_n-R⁸;

are aryl, arylcarbonyl, arylsulfonyl, hetaryl, hetaryl-
 carbonyl or hetarylsulfonyl, where these radicals may
 be partially or fully halogenated or may carry one to
 three of the following groups: cyano, nitro, hydroxyl,
 mercapto, amino, carboxyl, aminocarbonyl, aminothiocar-
 bonyl, halogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl,
 C₁-C₆-alkylcarbonyl, C₁-C₆-alkylsulfonyl,
 C₁-C₆-alkylsulfoxyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy,
 C₁-C₆-haloalkoxy, C₁-C₆-alkyloxycarbonyl,
 C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino,
 C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,
 hetaryl, hetaryloxy or C(=NOR⁷)-A_n-R⁸;

R⁵ is hydrogen,

is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, where the
 hydrocarbon radicals of these groups may be partially
 or fully halogenated or may carry one to three of the
 following radicals: cyano, nitro, hydroxyl, mercapto,



amino, carboxyl, aminocarbonyl, aminothiocarbonyl,
 halogen, C₁-C₆-alkylaminocarbonyl,
 di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 5 di-C₁-C₆-alkylaminothiocarbonyl, C₁-C₆-alkylsulfonyl,
 C₁-C₆-alkylsulfoxyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy,
 C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio, C₁-C₆-alkylamino,
 di-C₁-C₆-alkylamino, C₂-C₆-alkenyloxy, C₃-C₆-cycloalkyl,
 C₃-C₆-cycloalkyloxy, heterocyclyl, heterocyclyloxy,
 10 aryl, aryloxy, aryl-C₁-C₄-alkoxy, arylthio,
 aryl-C₁-C₄-alkylthio, hetaryl, hetaryloxy,
 hetaryl-C₁-C₄-alkoxy, hetarylthio,
 hetaryl-C₁-C₄-alkylthio, where the cyclic radicals for
 15 their part may be partially or fully halogenated and/or
 may carry one to three of the following groups: cyano,
 nitro, hydroxyl, mercapto, amino, carboxyl,
 aminocarbonyl, aminothiocarbonyl, C₁-C₆-alkyl,
 C₁-C₆-haloalkyl, C₁-C₆-alkylsulfonyl,
 C₁-C₆-alkylsulfoxyl, C₁-C₆-cycloalkyl,
 20 C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkoxycarbonyl,
 C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino,
 C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl,
 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 25 C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,
 arylthio, hetaryl, hetaryloxy, hetarylthio and
 C(=NOR⁷)-A_n-R⁸;

 is C₃-C₆-cycloalkyl, C₃-C₆-cycloalkenyl, heterocyclyl,
 30 aryl, hetaryl, where the cyclic radicals may be
 partially or fully halogenated or may carry one to
 three of the following groups: cyano, nitro, hydroxyl,
 mercapto, amino, carboxyl, aminocarbonyl,
 aminothiocarbonyl, halogen, C₁-C₆-alkyl,
 C₁-C₆-haloalkyl, C₁-C₆-alkylsulfonyl,
 35 C₁-C₆-alkylsulfoxyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy,
 C₁-C₆-haloalkoxy, C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylthio,
 C₁-C₆-alkylamino, di-C₁-C₆-alkylamino,
 C₁-C₆-alkylaminocarbonyl, di-C₁-C₆-alkylaminocarbonyl,
 40 C₁-C₆-alkylaminothiocarbonyl,
 di-C₁-C₆-alkylaminothiocarbonyl, C₂-C₆-alkenyl,
 C₂-C₆-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy,
 hetaryl and hetaryloxy;

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where



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A is oxygen, sulfur or nitrogen and where the nitrogen carries hydrogen or C₁-C₆-alkyl;

n is 0 or 1;

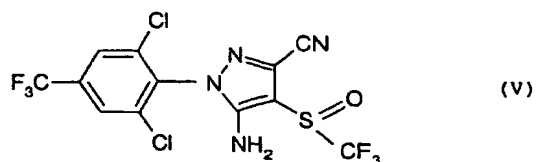
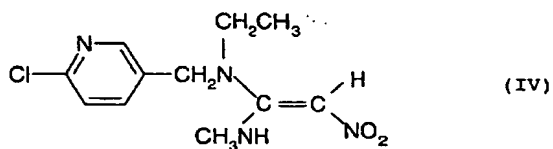
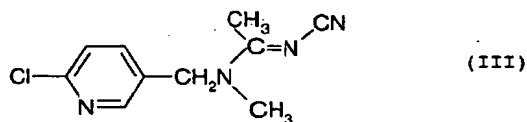
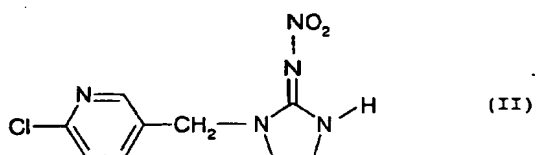
R⁷ is hydrogen or C₁-C₆-alkyl and

R⁸ is hydrogen or C₁-C₆-alkyl,

and their salts,

and

b) at least one compound of the formulae II to XI



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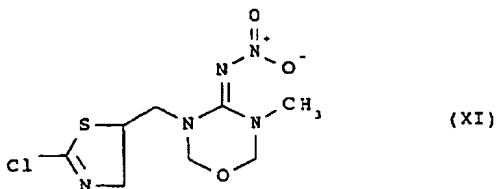
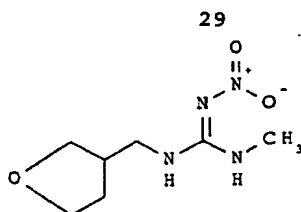
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in a synergistically effective amount.

2. A mixture as claimed in claim 1, which is conditioned in two parts, one part comprising the compound I in a solid or liquid carrier and the other part comprising at least one of the compounds II to XI in a solid or liquid carrier.
3. A method for controlling harmful fungi, which comprises treating the fungi, their habitat, or the materials, plants, seeds, soils, areas or spaces to be protected against fungal attack with a mixture as claimed in claim 1 or 2, where the application of the compound I and at least one of the compounds II to XI may be carried out simultaneously, either together or separately, or in succession.
4. A method as claimed in claim 3, wherein the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with from 0.005 to 1 kg/ha of a compound I as claimed in claim 1.
5. A mixture for crop protection substantially as hereinbefore described in examples I to IX.

DATED this 15th day of May, 2001

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Fungicidal mixtures based on tris(oxime ether) derivatives and insecticides

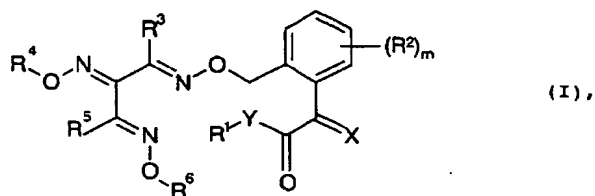
5 Abstract

Mixtures for crop protection, comprising as active components

a) phenylacetic acid derivatives of formula I

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in which the substituents and the index are each as defined in the description, and their salts,

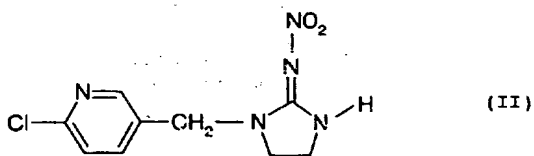
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and

b) at least one compound of the formulae II to XI

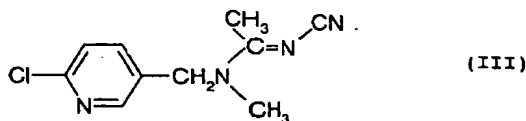
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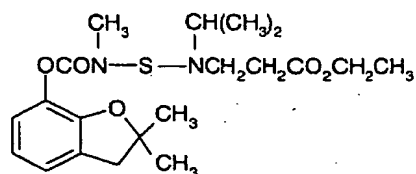
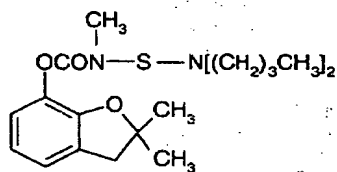
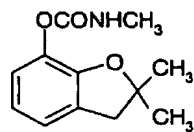
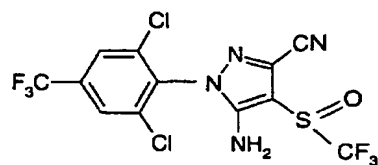
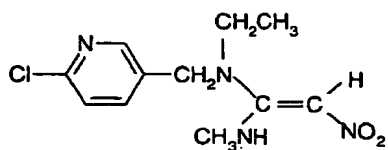


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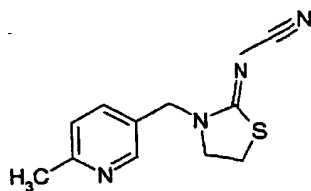
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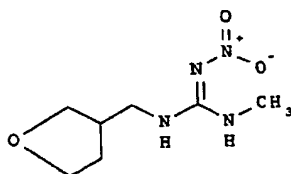
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(IX)

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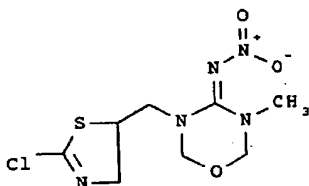
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(X)

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(XI)

in a synergistically effective amount.

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